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Kinetic Monte Carlo Simulations of Oxygen Diffusion in Environmental Barrier Coating Materials

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INTRODUCTION

Ceramic matrix composite (CMC) materials are under consideration for use in next-generation jet turbine engines. Such materials offer high melting temperatures, light weight, and good high-temperature strength, permitting increased operating temperatures and increased efficiencies. However, such components operate in an environment characterized not only by high temperatures, but by the presence of water vapor. Such an environment can lead to rapid corrosion, recession, and failure, unless steps are taken to protect the vulnerable components.

Ceramics coating systems, typically consisting of an Environmental Barrier Coating (EBC), a Thermal Barrier Coating (TBC), and a bond coat, are being developed to address this issue. Y and Yb-mono and disilicates are candidate materials for use in the EBC component of such systems, and the diffusive transport of water vapor and oxygen through these materials is of concern.

We have performed atomistic simulations of oxygen diffusivity, for β-$Yb_2Si_2O_7$, and δ- and γ-$Y_2Si_2O_7$, using the kinetic Monte Carlo (kMC) method. The migration barrier energies needed for the kMC simulations were computed using Density Functional Theory (DFT). We have also performed similar kMC simulations for hafnium silicate, $HfSiO_4$, a proposed bond coat material, to determine whether the bond coat provides additional protection against oxygen diffusion.

Structural information for high-temperature phases of all four materials is shown in Table 1.

Name	Crystal type	Space group	Atoms per cell	Distinct oxygen sites	*a*(expt),Å	*a*(DFT),Å
β-$Yb_2Si_2O_7$	Monoclinic	C2/m	22	3	6.802	6.825
γ-$Y_2Si_2O_7$	Monoclinic	$P2_1/C$	22	4	4.688	4.731
δ-$Y_2Si_2O_7$	Orthorhombic	$Pna2_1$	44	7	13.68	13.797
$HfSiO_4$	Tetragonal	$I4_1/amd$	24	1	6.573	6.609

Table—1 Structural information for candidate coating materials.

THEORY

The kMC method is aimed at the study of so-called infrequent-event systems. The kMC method is typically more efficient than molecular dynamics for the study of such systems.

Diffusive hopping is an example of an infrequent-event process; at all but the lowest temperatures it can be considered a thermally activated process that proceeds via the hopping of atoms among crystalline and interstitial sites.

A kMC diffusion simulation follows the trajectories of a series of random walkers, representing diffusing atoms, traversing a lattice, with each atomic site possessing a number of potential hopping paths.

- The hopping rate for each path is given by $\nu_{AB} = \nu^0 \exp(-E_{AB}/k_B T)$, in which ν_{AB} and E_{AB} are the hopping rate and migration barrier energy, respectively, and ν^0 is a frequency factor representative of atomic vibrational frequencies.
- The hopping probability for each path is calculated as $P_{AB} = \nu_{AB}/\Gamma$, in which Γ is the sum of hopping rates for all hops accessible to the system.
- One of the accessible hops is chosen stochastically and executed, with the diffusing atom moving to a nearby vacancy or interstitial site.
- The execution of the hop exposes a number of newly accessible hops, and renders some of the previously accessible ones no longer accessible, and the list of accessible hops is updated to incorporate the changes.
- The simulation clock is advanced stochastically by an amount consistent with the mean time between hops, $\Delta t = -\ln(R)/\Gamma$, with $0 < R \leq 1$ a random number.
- When a sufficient number of hops (4×10^{11} in this work) have been executed, the mean square displacement $\langle R^2 \rangle$ is computed, and the diffusivity obtained from the Einstein relation $\langle R^2 \rangle = 6\,D\,t$. A detailed description of the method is provided by Voter.
- For kMC simulations of vacancy-mechanism oxygen diffusion, it is convenient to track the motions of the relatively small number of vacancies, rather than the much larger number of oxygen atoms, yielding the vacancy diffusivity.
- The corresponding oxygen diffusivity can be obtained by distributing the vacancy displacements over the more numerous oxygen atoms by multiplying the vacancy diffusivity by a concentration correction factor $C_v/(1-C_v)$, in which C_v is the vacancy concentration.

DISCUSSION

- All energy calculations were performed using density functional theory (DFT) incorporating the plane-wave pseudopotential scheme, the Generalized Gradient Approximation, and the Projector Augmented Wave approach, as implemented in the VASP computer code.
- Lattice constants a were optimized while constraining b/a, c/a and all angles to their experimental values. As shown in Table 1, the values obtained for a are slightly larger than the experimental values, consistent with the Generalized Gradient Approximation's tendency to underbind.

Vacancy-mechanism diffusion

The ranges of vacancy formation energies for all materials are shown in Table 2. The values for Yb disilicate are smaller than those for the other materials, suggesting that the intrinsic vacancy concentration will be larger in that material. However, all vacancy formation energies are large enough that, for the range of temperatures considered here, the intrinsic vacancy concentrations for all materials will be very small, as will the concentration correction factors, and the diffusivity.

Migration barrier energies for oxygen diffusion via the vacancy mechanism were computed using the Improved Dimer Method included in the Transition State Tools suite of codes from the University of Texas. A large number of potential paths were investigated for each distinct oxygen site type for each material. Space limitations preclude a listing of all barrier energies for all materials, but the ranges of energies for each material are shown in Table 2. It can be seen that Yb disilicate has the smallest barrier energy.

Vacancy-mechanism oxygen diffusivities (assuming that only intrinsic vacancies are present) from kMC simulations, as functions of temperature, are shown in Figure 1. It can be seen that the diffusivities are largest for Yb disilicate; those of the two Y disilicate structures are substantially smaller. The presence of a small barrier (0.46eV) for Yb disilicate is a partial explanation for this, but the vacancy formation energies are considerably smaller, as well, and consequently the concentration correction factor for Yb disilicate are considerably larger.

Name	Vacancy formation energy range, eV	Barrier energy range, eV
β-$Yb_2Si_2O_7$	2.63-3.72	0.46-8.39
γ-$Y_2Si_2O_7$	5.15-5.48	1.80-8.15
δ-$Y_2Si_2O_7$	5.03-5.49	0.97-4.53
$HfSiO_4$	4.56	2.39-11.81

Table 2—Vacancy formation energies and vacancy-mechanism migration barrier energy ranges

The bond coat material, $HfSiO_4$, exhibits a range of barriers that is somewhat larger than those of the two Y disilicate polytypes, which should reduce the diffusivity. However, the vacancy formation energy lies below the ranges of the two Y disilicates, which serves to increase the diffusivity. The net result is a diffusivity curve that is very similar to those of the Y disilicates, suggesting that the bond coat can in fact offer a degree of additional protection.

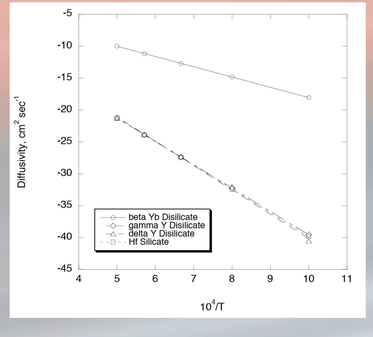

Figure 1.—Vacancy-mechanism oxygen diffusivity

The above diffusivities were computed under the assumption that only intrinsic vacancies were present. If a large number of extrinsic vacancies are present (as in Yttria-Stabilized Zirconia), the vacancy-mechanism diffusivities could be orders of magnitude larger.

INTERSTITIAL DIFFUSION

The structures of β-$Yb_2Si_2O_7$, γ-$Y_2Si_2O_7$, and $HfSiO_4$ are relatively open, containing channels through which interstitial oxygen diffusion might plausibly take place. Such a channel in β-$Yb_2Si_2O_7$ is shown in Figure 2.

We have performed migration barrier energy calculations, similar to those described above, for interstitial diffusion. A number of such channels were identified, and stable interstitial points located by relaxing interstitial oxygen atoms initially located along each such channel. Barriers for migration among these stable points were computed using the Improved Dimer method.

No attempt was made to identify all stable interstitial points, as the locations of these within, for example, distorted monoclinic structures can be difficult to determine. For this reason, kMC simulations of interstitial diffusion were not performed, although qualitative information can be obtained from the magnitudes of the migration barrier energies.

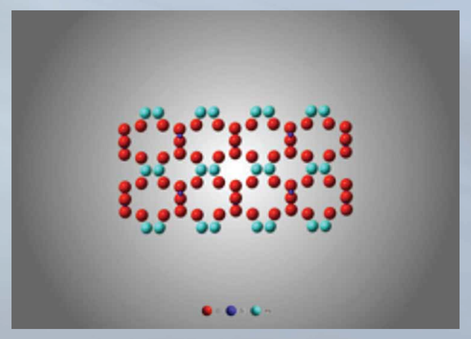

Figure 2.—Potential interstitial diffusion channels in β-$Yb_2Si_2O_7$

Because the number of interstitial atoms is typically much smaller than the number of interstitial sites, atomic displacements in the kMC simulations can be tracked directly, with no need for a concentration correction factor.

Interstitial migration barrier energy ranges for all materials except δ-$Y_2Si_2O_7$ are shown in Table 3. These values are somewhat smaller than those for vacancy diffusion, suggesting that the interstitial oxygen diffusivity will be somewhat larger than the vacancy diffusivity, and much larger than the vacancy-mechanism oxygen diffusivity, which does contain the concentration correction factor.

The structure of δ-$Y_2Si_2O_7$ is less open than those of the other three materials, and there are few plausible interstitial diffusion paths. Migration barrier calculations for two such paths indicate that the barriers are so large that interstitial diffusion will be negligible.

Material	Barrier energy range, eV
β-$Yb_2Si_2O_7$	1.03-3.50
γ-$Y_2Si_2O_7$	0.56-7.03
$HfSiO_4$	0.66-7.74

Table 3—Interstitial migration barrier energy ranges

Conclusions

- Vacancy-mechanism migration barriers for all four materials are large enough that, when only intrinsic vacancies are present, diffusivities from kMC simulations are very small.
- If large concentrations of extrinsic vacancies exist, the diffusivities can be orders of magnitude larger.
- Based on calculations of representative barrier calculations, interstitial diffusivities for β-$Yb_2Si_2O_7$, γ-$Y_2Si_2O_7$, and $HfSiO_4$ are likely to be large.
- The structure of δ-$Y_2Si_2O_7$ is considerably less open, and the representative barriers are large, suggesting that interstitial diffusion will be small.

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